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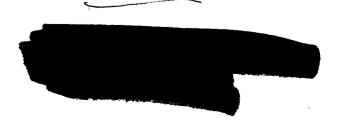
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In a recent paper under this title, Brattsev<sup>1</sup> has offered a proof that the energy of the ground state of a molecule (accurately) calculated in the Adiabatic Approximation is a <u>lower</u> bound to the true energy of the ground state. The purpose of the present note is two fold: First to correct a slight logical flaw in the proof, and secondly, to materially simplify the proof.

The difficulty with Brattsev's proof is that he apparently has not separated off the motion of the center of mass of the system. Thus his \(\psi\) is in fact a continuum wave function and therefore is not normalizeable, contrary to what he states. As is well known there are many ways of splitting off the motion of the center of mass. For definiteness sake, let us suppose we have referred the nuclear coordinates and the electronic coordinates to the center of mass of the nuclei. Then we may write the internal Hamiltonian as

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$$H = T_R + T_r + V(r,R)$$
 (1)

where  $T_R$  is the kinetic energy of the nuclei relative to their center of mass,  $T_r$  is the kinetic energy of the electrons relative to the center of mass of the nuclei, and V (r,R) is the potential energy.

The Adiabatic Approximation to the solution of  $H\psi = E\psi$  then reduces to the successive solution of the two equations

$$(T_r + V) \phi = \mathcal{E}(R) \phi$$
 (2)

$$(T_R + \mathcal{E}(R)) \gamma = E_A \gamma$$
 (3)

and we want to show 4 that

$$E \geqslant E_{\Delta}$$
 (4)

To do this we note that

$$E(\Psi, \Psi)_{R,r} = (\Psi, H \Psi)_{R,r}$$
 (5)

where we have put the subscripts on the scalar product symbol to remind ourselves that we are to integrate over both electronic (and sun over spins) and nuclear coordinates • We now observe that for fixed R

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$$(\Psi, (T_r + V)\Psi)_r \geqslant \mathcal{E}(R)(\Psi, \Psi)_r$$
 (6)

by the variational principle for equation (2). This then implies from (1) and (5) that

$$E(\psi, \psi)_{R,r} \geqslant (\psi, (T_R + \mathcal{E}(R))\psi)_{R,r}$$
 (7)

But now for fixed r

$$(\Psi, (T_R + \mathcal{E}(R))\Psi)_R \geqslant E_A(\Psi, \Psi)_R$$
 (8)

by the variational principle for equation (3), whence (7) becomes

$$E \geqslant E_A$$

which is what we set out to prove.

## FOCTNOTES

- V. F. Brattsev, Dckl. Akad. Nauk. SSSR <u>160</u>, 570 (1965)
   (English translation: Sov Phys.-Dokl. <u>10</u>, 44 (1965)).
- 2. See for example Jepsen and Hirschfelder, Proc. Nat. Acad. Sci. U.S.A. 45, 249 (1959) and J. Chem. Phys. 32, 1323 (1960).
- 3. We are using the same symbols as in reference 1 but with a slightly altered meaning.
- 4. As will be seen, the essential ingredient in the proof is that each term in H occurs in one and only one of the equations (2) and (3). This observation then permits ready generalization of the result (-) to other ways of separating the center of mass and other ways of defining the Adiabatic Approximation.